(19) Japan Patent Office (JP)

(12) Publication of Patent Application (A)

(11) Publication Number of Patent Application: 2002-324966

(P2002-324966A)

(43) Date of Publication of Application: November 8, 2002 (2002. 11. 8)

(51) Int. Cl.^{7} Identification Mark

H05K 3/10

B41J 2/01

C09D 5/24

201/00

F1		Theme Code (reference)
H05K 3/10	D	2C056
C09D 5/24		4J038
201/00		5E343
B41J 3/04	101 Z	

Request for Examination: Not made

Number of Claims: 10

OL

(Total Pages: 10)

(21) Application Number: 2001-125967 (P2001-125967)

(22) Application Date: April 24, 2001 (2001. 4. 24)

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(54) [Title of the Invention] Method for Forming Circuit Pattern Utilizing Inkjet Printing Method

(57) [Abstract]

[Problem] To provide a method for forming a novel circuit pattern which can form an ultrafine circuit pattern having excellent adhesion strength, a smooth surface contour, and low resistance, when an electrically conductive metal paste is inject-applied on a substrate or baked by utilizing an inkjet printing method.

[Means for Resolution] When plot-formation of a circuit pattern of a wiring substrate is performed by utilizing an inkjet

method, an electrically conductive metal paste to be used allows metal ultrafine particles having an average particle diameter of from 1 nm to 100 nm to be uniformly dispersed in a resin composition, wherein surfaces thereof are coated with one or more types of compounds each containing a group having nitrogen, oxygen and sulfur atoms as a group capable of bonding with an metal element in a coordinate manner, the resin composition contains a thermosetting resin component which functions as an organic binder, a component which, when heated, comes to have reactivity with the group having nitrogen, oxygen and sulfur atoms, and at least one type of organic solvent.

[Claims]

[Claim 1] A method for forming a circuit pattern by utilizing an inkjet printing method, the former method being a method for performing plot-formation of the circuit pattern of a wiring substrate by using an electrically conductive metal paste by utilizing an inkjet method,

wherein the electrically conductive metal paste to be used is an electrically conductive metal paste in which metal ultrafine particles having a very small average particle diameter are uniformly dispersed in a resin composition containing an organic solvent, the metal ultrafine particles having a very small average particle diameter are selected such that the average particle diameter thereof is in the range of

from 1 nm to 100 nm, and surfaces of the metal ultrafine particles are coated by at least one type of compound containing a group having nitrogen, oxygen and sulfur atoms as a group capable of bonding with a metal element contained in the metal ultrafine particles in a coordinate manner,

the method for forming the circuit pattern by using the inkjet printing method, being characterized by comprising the steps of:

inject-applying the electrically conductive metal paste on a substrate as a fine droplet by a plotting means of the inkjet method to plot the circuit pattern comprising a coating film of the thus plotted electrically conductive metal paste; and

thermally treating the coating film of the electrically conductive metal paste at a temperature at which at least the thermosetting resin is thermally cured.

[Claim 2] The method for forming the circuit pattern as set forth in Claim 1, wherein the resin composition is characterized by comprising a thermosetting resin component which functions as an organic binder, a component which, when heated, comes to have reactivity with the group having the nitrogen, oxygen and sulfur atoms against at lest one type of compound containing the group having the nitrogen, oxygen and sulfur atoms, and at least one type of organic solvent.

[Claim 3] The method for forming the circuit pattern as set forth in Claim 2, being characterized by comprising, in the step of plotting the circuit pattern, the steps of:

inject-applying a liquid in which metal ultrafine particles coated with at least one type of compound containing the group having the nitrogen atom, an oxygen atom and the sulfur atom are dispersed in the organic solvent, a liquid comprising the thermosetting resin component constituting the resin composition, the component having reactivity with the group having the nitrogen, oxygen and sulfur atoms, and the organic solvent on the substrate by utilizing individual plotting means of the inkjet method;

mixing both of the liquids on the substrate; and

forming the coating film made of the electrically conductive metal paste.

[Claim 4] The method for forming the circuit pattern as set forth in Claim 1 or 3, being characterized by using an organic acid anhydride, a derivative thereof or an organic acid as a component having reactivity with the group having the nitrogen, oxygen and sulfur atoms.

[Claim 5] The method for forming the circuit pattern as set forth in Claim 1 or 3, being characterized in that the metal

ultrafine particles having a very small average particle diameter contained in the electrically conductive metal paste are fine particles comprising one type of metal or fine particles of an alloy made of two or more types of metals selected from the group consisting of: gold, silver, copper, platinum, palladium, tungsten, nickel, tantalum, bismuth, lead, indium, tin, zinc, titanium, and aluminum.

[Claim 6] The method for forming the circuit pattern as set forth in Claim 1 or 3, being characterized in that, in the thermally treating step to be performed at a temperature at which at least the thermosetting resin is thermally cured, the metal ultrafine particles contained in the electrically conductive paste in the plotted coating film are further baked thereamong.

[Claim 7] The method for forming the circuit pattern as set forth in Claim 1 or 3, being characterized in that the plotting means of the inkjet method is a plotting means of a thermal method which generates air bubbles by performing thermal-foaming to discharge a droplet and at least one type of organic solvent contained in the electrically conductive metal paste to be used is such that a boiling point thereof is lower than a heating temperature of the thermal-foaming.

[Claim 8] The method for forming the circuit pattern as set forth in Claim 1 or 3, being characterized in that the plotting means of the inkjet method is a plotting means of a piezo method which discharges the droplet by performing compression utilizing a piezo element, and at least one type of organic solvent contained in the electrically conductive metal paste to be used is such that a boiling point thereof is lower than the temperature at which at least the thermosetting resin is thermally cured.

[Claim 9] The method for forming the circuit pattern as set forth in Claim 1 or 3, being characterized in that the resin composition containing the organic solvent is contained in the range of from 50 parts by mass to 300 parts by mass with the organic solvent being contained in the range of from 20 parts by mass to 270 parts by mass therein in the electrically conductive metal paste, per 100 parts by mass of the metal ultrafine particles in each case.

[Claim 10] The method for forming the circuit pattern as set forth in Claim 3, being characterized in that the thermosetting resin component, which functions as the organic binder, to be used in the resin composition is a thermosetting resin which can thermally be polymerized by using the organic acid anhydride, the derivative thereof or the organic acid as a polymerization

agent.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs] The present invention relates to a method for forming a circuit pattern by using an electrically conductive metal paste by utilizing an inkjet printing method and, more particularly, relates to a method for forming an extremely fine circuit patter having low impedance corresponding to digital high density wiring on a rigid or flexible printed circuit board, an IC chip, a glass substrate, a ceramic substrate or the like by using an electrically conductive metal paste for an ultrafine printing by utilizing an inkjet printing method.

[0002]

[Prior Art] As a method for plot-forming a circuit pattern on a printed wiring board, an electrically conductive metal paste is in most cases applied by screen printing, particularly, using a metal mask and, then, thermally cured to form a desired circuit pattern having low resistance. Such plotting method utilizing a screen printing method is widely adopted in a field in which line width of the circuit pattern to be formed is not extremely small and, as the electrically conductive metal paste to be used, an electrically conductive metal paste in which metal

powders having an average particle diameter of from 0.5 μm to 20 μm are dispersed in a thermosetting resin composition is used. Further, film thickness of the circuit pattern to be plotted is selected in correspondence with a minimum line width to be formed such that a ratio of film thickness/minimum line width and an aspect ratio thereof do not come to be extremely small.

[0003] On the other hand, along with a recent rapid trend of downsizing an information terminal, a wiring pitch on a printed wiring board to be mounded thereon has become narrower and, specifically, along with a trend of allowing a circuit inside a semiconductor to be finer, the minimum line width and the film thickness of the circuit pattern to be formed on the printed wiring board have become more and more small. For example, in a case in which the film thickness is several microns, when a conventional metal paste in which metal powders having an average particle diameter of 0.5 μm or more are used is utilized, the particle diameter of the metal powders to be contained becomes relatively unduly large whereupon the conventional metal paste can not sufficiently correspond to the case. Specifically, only 2 or 3 metal particles are sometimes present in a direction of thickness which is several microns and, as a result, a film thickness distribution becomes relatively large whereupon variance of conductivity sometimes becomes

conspicuous. Further, when only several metal particles are present, a partial loss of contacts among metal particles becomes a factor of substantially reducing conductivity.

[0004] Still further, a limitation is put on reduction of the film thickness since the metal mask itself to be used in the screen printing maintains itself a desired mechanical strength based on a structure thereof whereupon a limitation is spontaneously put on width between circuits adjacent to each other in accordance with thickness of the metal mask itself. Take, for example, a case in which a high density electronic part having a space of 0.3 mm or less between any two circuits is aimed to be actually mounted. It becomes difficult to perform plotting of the circuit pattern by utilizing the screen printing method with high reproducibility. On the other hand, in a plotting method of the inkjet method or a method for discharging the metal paste by utilizing a nozzle or a needle, direct plotting is performed by using the metal paste which is injected in minute droplet form whereupon a plottable minimum line width and a minimum space between circuits depend only on a quantity of the metal paste in droplet form to be inject-applied. Therefore, by allowing the metal paste to be injected in droplet form to be minute in size, it becomes possible to selectively apply the metal paste only in an extremely small area whereupon, for example, it becomes possible to apply the metal paste for

production of the high density circuit pattern having a space of 0.3 mm or less between any two circuits.

[0005] Further, in a case in which the plotting method of the inkjet method is utilized, even when a circuit pattern shape is complicated, for example, a portion of fine line width and a region of wide solid print are present in a mixed state, since the film thickness is theoretically determined only by a quantity of the metal paste to be applied in droplet form per unit area, it becomes possible to attain high uniformity of the film thickness. Still further, on this occasion, for example, in a case in which the film thickness comes down to several microns, when the conventional metal paste utilizing the metal powers having an average particle diameter of 0.5 μm or more is employed, the particle diameter of the contained metal powders becomes relatively large in a same manner as in the screen printing method described above whereupon the conventional metal paste can not sufficiently correspond to the case.

[0006]

[Problems that the Invention is to Solve] Under these circumstances, when the plotting method of the inkjet method is utilized in forming the circuit patter, in order to fully perform a high plotting resolution thereof, it is necessary

to allow the particle diameter of each of the metal powders to be contained as the electrically conductive metal paste to be utilized to be sufficiently fine. For example, it is necessary to utilize the electrically conductive metal paste containing metal ultrafine particles each having an extremely small particle diameter as an electrically conductive metal paste to be utilized.

[0007] As one method for producing metal ultrafine particles each having a very small particle diameter, namely, metal ultrafine particles having at least an average particle diameter of 100 nm or less, a dispersion of the metal ultrafine particles of 10 nm or less in colloidal form which is prepared by using an evaporation-in-gas method and a production method thereof are disclosed in JP-A No. 3-34211. Further, a dispersion of the metal ultrafine particles having an average particle diameter in the range of from several nm to ten times several nm in colloidal form prepared by utilizing a reduction-precipitation method which uses an amine compound for performing such reduction and a production method thereof are disclosed in JP-A No. 11-319538 and the like. The metal ultrafine particles having an average particle diameter of several nm to 10 times several nm disclosed in JP-A No. 11-319538 and the like are such that surfaces thereof are coated with a polymer resin or the like to maintain the colloidal form.

[0008] In a case in which the metal paste constituted by the metal fine particles having an average particle diameter as extremely fine as from 1 nm to 100 nm is utilized, even when a fine line width and a small film thickness are adopted, it is possible to substantially reduce an extent of unevenness of such thickness to be theoretically caused by particle diameters of the metal particles to be used. It is desired, while making use of such advantages, to utilize the electrically conductive metal paste containing the metal ultrafine particles having an average particle diameter of from several nm to 10 times several nm in forming the circuit pattern by the plotting method of the inkjet method. In other words, on condition that an electrically conductive metal paste containing metal ultrafine particles in a form which facilitates the use of the plotting method of the inkjet method is first prepared, development of a method for forming the circuit pattern by utilizing the inkjet printing method which uses the thus-prepared electrically conductive metal paste is desired.

[0009] It is known that the metal ultrafine particles having an average particle diameter of from several nm to 10 times several nm can ordinarily be baked at a temperature by far lower than the melting point thereof (for example, 200°C in a case of silver). Such low-temperature baking can be

performed, due to the fact that, when a particle diameter of each of metal ultrafine particles is allowed to be sufficiently small, a ratio of atoms in a high energy state present on a particle surface against entire atoms becomes large whereupon a surface diffusion of metal atoms becomes too large to be neglected and, as a result, an extension of an interface between particles is conducted based on the surface diffusion thereof, thereby allowing the baking to be performed. On the other hand, owing to such property as described above, when surfaces of metal ultrafine particles are directly contacted thereamong even at a temperature in the neighborhood of room temperature, a phenomenon of forming an agglomerated body occurs. Such formation of the agglomerated body becomes a factor of impairing an effect of enhancing uniformity of thickness which can be achieved as a result of the fact that the metal ultrafine particles which are extremely fine in size are formed in a densely packed state. Further, incorporation of a structure, in which the agglomerated body has previously been partially formed, becomes a cause which prevents an effect that a desired electric conductivity is achieved as a whole by forming the densely packed state from being attained with high reproducibility of such densely packed state.

[0010] Still further, the surface diffusion of metal atoms on the surfaces of the metal ultrafine particles is more active

than that on a surface of an ordinary metal aggregate and, also, chemical reactivity thereon is also increased compared with that on the surface of the ordinary metal aggregate whereupon, for example, surface oxidation progresses faster upon exposure to oxygen thereon. On this occasion, a merit of the low-temperature baking on the surfaces of metal ultrafine particles is impaired whereupon a state in which baking of ultrafine particles thereamong can be attained is realized only by performing a heating treatment at a relatively high temperature necessary for removing an influence of oxide film formed by the surface oxidation. Therefore, the oxide film to be formed, though depending on an extent thereof, is a factor for generating variation of the electrical conductivity.

[0011] Particularly, when the electrically conductive metal paste containing the metal ultrafine particles is inject-applied by utilizing the inkjet method, uniformity of the quantity of the metal ultrafine particles contained in a fine droplet to be discharged is indispensable. Namely, it is also an essential requirement that the metal ultrafine particles contained in the electrically conductive metal paste are in a state in which they are uniformly dispersed in a dispersion solvent. Specifically, it is also necessary to suppress a phenomenon in which the metal ultrafine particles are agglomerate-separated or precipitate-separated or the like

while they are kept in a container attached to the inkjet printer head to be used. Further, it goes without saying that a situation in which an agglomerated body of the metal ultrafine particles generated by agglomeration of the metal ultrafine particles is adhered to a discharge nozzle tip or the like of the inkjet printer head must be prevented. A method, for forming the circuit pattern by utilizing the inkjet method using the electrically conductive metal paste containing the metal ultrafine particles, which can avoid an inherent problem in utilization of the inkjet method and attain not only high uniformity of film thickness but also excellent conductivity is desired to be developed.

[0012] The present invention is to solve the above-described problems and has an object to provide a method, for forming a circuit pattern by utilizing a novel inkjet printing method, which can form an ultrafine circuit pattern having excellent adhesion strength, a smooth surface contour, and low resistance, when, while suppressing formation of the agglomerated body or precipitate-separation of contained metal ultrafine particles in storage by using metal Ultrafine particles as an electrically conductive medium which constitutes an electrically conductive metal paste, the electrically conductive metal paste in which the metal ultrafine particles are uniformly dispersed is inject-applied on a

substrate or baked by utilizing the inkjet printing method.

[0013]

[Means for Solving the Problems] As a result of an extensive study executed by the present inventors to solve the above-described problems, it was found that, in a case in which metal ultrafine particles having an average particle diameter of from 1 nm to 100 nm are used as an electrically conductive medium which constitutes an electrically conductive metal paste, when the electrically conductive metal paste itself is prepared, a stabilized colloidal state is advantageous in enhancing agglomeration resistance; however, at the time a thermosetting resin contained as a binder component is thermally cured and, on that occasion, when a molecular layer covering each of surfaces of metal ultrafine particles which contributes to maintaining the colloidal state remains as it is, fusion of contact interface to be derived from baking at a low temperature among metal ultrafine particles which is indispensable for attaining excellent electric conductivity is liable to be impaired. As a result of further study and research executed by the present inventors at such finding, it was also found that, in a constitution in which, although a molecular layer covering each of the surfaces of the metal ultrafine particles which contributes to maintaining the stabilized colloidal state during a period of time in which the electrically conductive

metal paste itself is prepared and, then, stored at a temperature in the neighborhood of room temperature is provided, the molecular layer covering each of the surfaces can effectively be removed at the time the thermosetting resin of the law temperature curing type is thermally cured, it becomes possible to maintain sufficiently high electric conductivity imparted to a thin film wiring pattern to be formed and also high reproducibility thereof, while maintaining sufficient adhesion to a substrate by a thermosetting resin (organic binder) component which has been thermally cured at an appropriate temperature, smoothness of a surface contour by using the metal ultrafine particles which are uniformly dispersed in a colloidal state, and also a merit of an ultrafine circuit-plotting property by the inkjet method.

[0014] Namely, the method for forming the circuit pattern by utilizing the inkjet printing method according to the invention is a method for performing plot-formation of the circuit pattern of a wiring substrate by using an electrically conductive metal paste by utilizing an inkjet method, wherein the electrically conductive metal paste to be used is an electrically conductive metal paste in which metal ultrafine particles having a very small average particle diameter are uniformly dispersed in a resin composition containing an organic solvent, the metal ultrafine particles having a very small

average particle diameter are selected such that the average particle diameter thereof is in the range of from 1 nm to 100 nm, and surfaces of the metal ultrafine particles are coated by at least one type of compound containing a group having nitrogen, oxygen and sulfur atoms as a group capable of bonding with a metal element contained in the metal ultrafine particles in a coordinate manner,

the method for forming the circuit pattern by using the inkjet printing method, being characterized by comprising the steps of:

inject-applying the electrically conductive metal paste on a substrate as a fine droplet by a plotting means of the inkjet method to plot the circuit pattern comprising a coating film of the electrically conductive metal paste; and

thermally treating the plotted coating film of the electrically conductive metal paste at a temperature at which at least the thermosetting resin is thermally cured. On this occasion, it is preferable that the resin composition comprises a thermosetting resin component which functions as an organic binder, a component which, when heated, comes to have reactivity with the group having the nitrogen, oxygen and sulfur atoms against at lest one type of compound containing the group having the nitrogen, oxygen and sulfur atoms, and at least one type of organic solvent.

[0015] Further, there can be provided the method for forming the circuit pattern characterized by comprising, in the step of plotting the circuit pattern, the steps of:

inject-applying a liquid in which metal ultrafine particles coated with at least one type of compound containing the group having the nitrogen atom, an oxygen atom and the sulfur atom are dispersed in the organic solvent, a liquid comprising the thermosetting resin component constituting the resin composition, the component having reactivity with the group having the nitrogen, oxygen and sulfur atoms, and the organic solvent on the substrate by utilizing individual plotting means of the inkjet method;

mixing both of the liquids on the substrate; and

forming the coating film made of the electrically conductive metal paste. Still further, it is preferable that an organic acid anhydride, a derivative thereof or an organic acid is used as a component having reactivity with the group having the nitrogen, oxygen and sulfur atoms.

[0016] On the other hand, there can be provided the method for forming the circuit pattern characterized in that the metal ultrafine particles having a very small average particle diameter contained in the electrically conductive metal paste are fine particles comprising one type of metal or fine particles of an alloy made of two or more types of metals selected from

the group consisting of: gold, silver, copper, platinum, palladium, tungsten, nickel, tantalum, bismuth, lead, indium, tin, zinc, titanium, and aluminum.

[0017] Further, in the method for forming the circuit pattern according to the invention, in the thermally treating step to be performed at a temperature at which at least the thermosetting resin is thermally cured, the metal ultrafine particles contained in the electrically conductive metal paste in the plotted coating film can further be baked thereamong; such case is preferable.

[0018] There can be provided the method for forming the circuit pattern characterized in that, for example, the plotting means of the inkjet method is a plotting means of a thermal method which generates air bubbles by performing thermal-foaming to discharge a droplet and at least one type of organic solvent contained in the electrically conductive metal paste to be used is such that a boiling point thereof is lower than a heating temperature of the thermal-foaming. Alternatively, there can be provided the method for forming the circuit pattern characterized in that the plotting means of the inkjet method is a plotting means of a piezo method which discharges the droplet by performing compression utilizing a piezo element, and at least one type of organic solvent contained

in the electrically conductive metal paste to be used is such that a boiling point thereof is lower than the temperature at which at least the thermosetting resin is thermally cured.

[0019] It is preferable that the resin composition containing the organic solvent is contained in the range of from 50 parts by mass to 300 parts by mass with the organic solvent being contained in the range of from 20 parts by mass to 270 parts by mass therein in the electrically conductive metal paste to be used for forming the circuit pattern, per 100 parts by mass of the metal ultrafine particles in each case.

[0020] It is preferable that, in the method for forming the circuit pattern according to the invention, the thermosetting resin component, which functions as the organic binder, to be used in the resin composition is a thermosetting resin which can thermally be polymerized by using the organic acid anhydride, the derivative thereof or the organic acid as a polymerization agent.

[0021]

[Mode for Carrying Out the Invention] Hereinafter, the method for forming the circuit pattern by utilizing the inkjet printing method according to the invention will be described in detail.

[0022] Since a major application of the method for forming the circuit pattern according to the invention is ultrafine printing for use in circuit formation, or interlayer contact formation which has low impedance corresponding to digital high density wiring and is extremely fine by using printing in a minimal dot state which has not easily been plotted with high reproducibility by a conventional screen printing method or a dispense printing method, metal ultrafine particles to be contained as an electrically conductive medium are such that an average particle diameter thereof is selected, in accordance with a targeted line width of an ultrafine printing and film thickness after thermally cured, to be in the range of from 1 nm to 100 nm and, preferably, in the range of from 2 nm to 10 nm.

[0023] As described above, in using the extremely fine metal ultrafine particles, when the metal particles are allowed to contact thereamong even in a state in which they are soaked in a dispersion solvent, individual metal ultrafine particles are adhered thereamong to generate agglomeration and the resultant agglomerated body is not suitable for ultrafine printing which the invention aims for. In order to prevent such agglomeration among particles, the metal ultrafine particles in a state in which, after surfaces thereof are

provided with a low-molecular coating layer, they are dispersed in a solution in which a thermosetting resin component is dissolved are utilized.

[0024] Further, in the method for forming the circuit pattern according to the invention, with reference to the electrically conductive metal paste applied on the substrate, when the contained thermosetting resin component is thermally cured, an electrically conductive metal paste in a state in which an oxide film is substantially absent on the surfaces of the metal ultrafine particles such that the metal ultrafine particles as the electrically conductive medium are allowed to be fused thereamong at a contact interface thereof is utilized. Specifically, although an oxide film is absent on the surfaces of the metal ultrafine particles themselves by allowing the surfaces thereof to be covered by at least one type of compound which contains a group having nitrogen, oxygen and sulfur atoms as a group capable of bonding in a coordinate manner with a metal element contained in the metal ultrafine particles, the metal ultrafine particles come to be in a state in which the metal surfaces are not allowed to directly contact thereamong.

[0025] The compound to be utilized for covering such surface utilizes a group having a lone electron pair present on each of the nitrogen, oxygen, and sulfur atoms, when the

compound forms a bond with a metal element in a coordinate manner, whereupon, for example, an amino group is mentioned as a group having a nitrogen atom. Further, as a group having a sulfur atom, a sulfanyl group (-SH), and a sulfane-diyl group (-S-) of sulfido type are mentioned. Still further, as a group having an oxygen atom, a hydroxyl group, and an oxy group (-O-) of ether type are mentioned.

[0026] As a representative example of the compound having an available amino group, an alkyl amine can be mentioned. Further, the alkyl amine which is not removed under an ordinary storage environment, specifically, in the range of less than 40°C in a state of forming a bond with a metal element in a coordinate manner is favorable whereupon the alkyl amine which has a boiling point in the range of 60°C or more and, preferably, 100°C or more is preferable. However, when baking/alloying is performed, it is necessary to allow the alkyl amine to be quickly removed from the surface whereupon the alkyl amine which has a boiling point in the range of at least 300°C or less and, ordinarily, 250°C or less is preferable. For example, as an alkyl group of the alkyl amine, the alkyl group of from C_4 to C_{20} is used and, more preferably, the alkyl group is selected such that it is in the range of from C_8 to C_{18} whereupon the alkyl group having an amino group at a terminal of an alkyl chain thereof is used. For example, the alkyl amine in the

range of from C_8 to C_{18} is thermally stable, a vapor pressure thereof is not unduly high and, when the alkyl amine is stored at room temperature, it is easy to maintain/control a content ratio thereof in a desired range and the like whereupon such alkyl amine is favorably used from the standpoint of convenience of handling. Ordinarily, from the standpoint of forming a bond in such coordinate manner, a compound of primary amine type exhibits high bonding ability and, accordingly, is favorable; however, compounds of secondary amine type and tertiary amine type are also usable. Further, compounds of 1,2-diamine type, 1,3-diamine type and the like in which adjacent 2 or more amines are related with bonding are also usable.

[0027] Further, as a representative example of a compound having an available sulfanyl group (-SH), an alkane thiol can be mentioned. Still further, the alkane thiol which is not removed under an ordinary storage environment, specifically, in the range of less than 40°C in a state of forming a bond with a metal element in a coordinate manner is also favorable whereupon the alkane thiol which has a boiling point in the range of 60°C or more and, preferably, 100°C or more is preferable. However, when baking/alloying is performed, it is necessary to allow the alkane thiol to be quickly removed from the surface whereupon the alkane thiol which has a boiling point in the range of at least 300°C or less and, ordinarily, 250°C or less

is preferable. For example, as an alkyl group of the alkane thiol, an alkyl group of from C_4 to C_{20} is used and, more preferably, the alkyl group is selected such that it is in the range of from C_8 to C_{18} whereupon the alkyl group having a sulfanyl group (-SH) at a terminal of an alkyl chain thereof is used. For example, the alkane thiol in the range of from C_8 to C_{18} is thermally stable, a vapor pressure thereof is not unduly high and, when the alkane thiol is stored at room temperature, it is easy to maintain/control a content ratio thereof in a desired range and the like whereupon such alkane thiol is favorably used from the standpoint of convenience of handling. Ordinarily, a compound of primary thiol type exhibits high bonding ability and, accordingly, is favorable; however, compounds of secondary thiol type and tertiary thiol type are also usable. Further, compounds of 1,2-dithiol type and the like in which adjacent 2 or more sulfanyl groups (-SH) are related with bonding are also usable.

[0028] Further, as a representative example of a compound having an available hydroxyl group, an alkane diol can be mentioned. Still further, the alkane diol which is not removed under an ordinary storage environment, specifically, in the range of less than 40°C in a state of forming a bond with a metal element in a coordinate manner is also favorable whereupon the alkane diol which has a boiling point in the range of 60°C

or more and, preferably, 100°C or more is preferable. However, when baking/alloying is performed, it is necessary to allow the alkane diol to be quickly removed from the surface whereupon the alkane diol which has a boiling point in the range of at least 300°C or less and, ordinarily, 250°C or less is preferable. For example, compounds of 1,2-diol type and the like in which 2 or more hydroxyl groups are related with bonding can favorably be used.

[0029] Further, in the method for forming the circuit pattern according to the invention, a thermosetting resin component which functions as an organic binder is contained in the electrically conductive metal paste to be utilized as an essential component. The thermosetting resin component has functions for allowing contained metal ultrafine particles to contact with one another and imparting adhesion to a substrate, when applied electrically conoductive metal paste is thermally cured. Therefore, an organic binder or a thermosetting resin which is utilized in an ordinary electrically conductive metal paste can be utilized. For example, one or more types of resin components which are sufficiently cured by a heating treatment at a targeted thermosetting temperature may be selected among, for example, the thermosetting resin components exemplified below in accordance with such targeted thermosetting temperature. Examples of such thermosetting resins include

a phenol resin, an epoxy resin, an unsaturated polyester resin, a vinyl ester resin, a diallyl phthalate resin, an origoester acrylate resin, a xylene resin, a bismaleimido triazine resin, a furan resin, a urea resin, a polyurethane resin, a melamine resin, and a silicone resin. A phenol resin and an epoxy resin thereamong are favorable as a resin component to be utilized in the invention, since these resins are excellent in adhesion at the time of forming ultrafine circuit and the properties thereof after being cured are suitable for the electrically conductive paste.

[0030] A quantity of each of these thermosetting resin components to be contained is appropriately selected in accordance with a ratio of an entire volume of the metal ultrafine particles to spaces present among such particles; however, it may be selected in the range of ordinarily from 1 part by mass to 30 parts by mass and, preferably, from 3 parts by mass to 20 parts by mass, per 100 parts by mass of the metal ultrafine particles in each case. In addition to the thermosetting resin which functions as the organic binder, a component which, when heated, comes to have reactivity with a group having nitrogen, oxygen and sulfur atoms against at least one type of compound containing the above-described group having the nitrogen, oxygen and sulfur atoms which form a molecular layer covering the surfaces of the metal ultrafine particles, for example,

an organic acid anhydride, a derivative thereof or an organic acid and, preferably, an acid anhydride or a derivative thereof, is allowed to be contained.

[0031] This component which has reactivity with the group having the nitrogen, oxygen and sulfur atoms, for example, the acid anhydride or the derivative thereof, is primarily utilized for removing an adhesion layer, derived from the compound containing the group having the nitrogen, oxygen and sulfur atoms as a group capable of bonding with an metal element in a coordinate manner, which covers surfaces of the metal ultrafine particles. That is, when heated, the component reacts with the group having the nitrogen, oxygen and sulfur atoms contained in the compound which forms the adhesion layer at a temperature in the neighborhood of room temperature and, as a result, after such reaction, the group having the nitrogen, oxygen and sulfur atoms becomes difficult to form a bond with metal atoms on the surfaces in a coordinate manner on the surfaces of the metal ultrafine particles, thereby resulting in being removed. Such removal function is not executed until formation of the coating film of the electrically conductive metal paste is completed and, thereafter, the function is executed only in a heating step in which the contained thermosetting resin component is thermally cured. Further, in a case in which the thermosetting resin to be used is an epoxy resin or the like, the acid anhydride

or the derivative thereof for use in such purpose sometimes becomes a hardener thereof. In such case, at the time of thermosetting, the acid anhydride or the derivative thereof is utilized not only for reacting with the compound containing the group having the nitrogen, oxygen and sulfur atoms, for example, an amine compound, a thiol compound, a diol compound or the like to form an amide, a thio ester, or an ester, but also for being consumed as a hardener for an epoxy resin or the like. Therefore, the acid anhydride or the derivative thereof may be added in a quantity more than a quantity thereof to be added which is determined in accordance with a sum of a terminal amino group, the sulfanyl group (-SH) and the hydroxyl group contained in the amine compound, the thiol compound, the diol compound or the like. Further, since, for example, the terminal amino group of the amine compound also reacts with the epoxy resin and the like, the quantity of the acid anhydride or the derivative thereof to be contained is appropriately selected not only in accordance with the type and the quantity to be contained of the alkyl amine and the like, but also by taking into consideration the type and reactivity of the thermosetting resin to be utilized.

[0032] Therefore, when the thermosetting resin component is thermally cured, the compound covering the surfaces of the metal ultrafine particles is allowed to be removed in a thermal

manner and also allowed to react with a component having reactivity with the group having the nitrogen, oxygen and sulfur atoms, for example, the acid anhydride or the derivative thereof to efficiently remove the coating layer whereupon the metal ultrafine particles are allowed to directly contact with one another. As a result, along with curing of the thermosetting resin component, baking at a low temperature which is an inherent property of the metal ultrafine particles proceeds and, as a whole, fusion by the baking in a state in which the metal ultrafine particles are densely packed can be attained whereupon a conduction path in a dense network state to be formed imparts an excellent electric conductivity.

[0033] The organic acid anhydride, the derivative thereof or the organic acid to be utilized is not particularly limited so long as it exhibits the reactivity. Examples of utilizable organic acids include various types of carboxylic acids including linear or branched saturated carboxylic acids of from C_1 to C_{10} such as formic acid, acetic acid, propionic acid, butanoic acid, hexanoic acid, and octylic acid; unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, benzoic acid, and sorbic acid; dibasic acids such as oxalic acid, malonic acid, sebacic acid, maleic acid, fumaric acid, and itaconic acid; and other organic acids such as a phosphoric acid ester and a sulfonic acid which

contain a phosphoric acid group ($-O-P(O)(OH)_2$) or a sulfo group ($-SO_3H$) in place of the carboxylic group.

[0034] Further, examples of favorably utilizable organic acid anhydrides or derivatives thereof include aromatic acid anhydrides such as phthalic acid anhydride, trimellitic acid anhydride, pyromellitic acid anhydride, benzophenone tetracarboxylic acid anhydride, ethylene glycol bis(anhydrotrimellitate) and glycerol tris(anhydrotrimellitate); cycloaliphatic acid anhydrides such as maleic acid anhydride, succinic acid anhydride, tetrahydrophphalic acid anhydride, methyl tetrahydrophthalic acid anhydride, methyl nadic acid anhydride, an alkenyl succinic acid anhydride, hexahydrophthalic acid anhydride, methyl hexahydrophthalic acid anhydride, and methyl cyclohexene tetracarbxylic acid anhydride; and aliphatic acid anhydrides such as a polyadipic acid anhydride, a polyazelaic acid anhydride, and polysebacic acid anhydride. Among these acid anhydrides, methyl tetrahydrophthalic acid anhydride, methyl hexahydrophtahlic acid anhydride and respective derivatives thereof have appropriate reactivity against, for example, a terminal amino group of the amine compound at a relatively low thermosetting temperature which the invention aims for and are favorably used.

[0035] In the method for forming the circuit pattern according to the invention, although the electrically conductive metal paste to be utilized is subjected to a heat-curing treatment after applied, the electrically conductive metal paste is, when it is applied, allowed to be an electrically conductive metal paste in which the metal ultrafine particles in which the surfaces thereof are provided with the molecular coating layer are uniformly dispersed in the resin composition in solution form, namely, the solution as a dispersion medium comprising the thermosetting resin component which functions as the organic binder, the component which has reactivity, when heated, with the group having the nitrogen, oxygen and sulfur atoms, for example, the organic acid anhydride, the derivative thereof or the organic acid, and at least one type of organic solvent. As for the organic solvent to be utilized on this occasion, an organic solvent which has a function as a solvent when the resin composition is prepared and prevents the adhesion layer of a compound, such as an amine compound covering the surface of each of the metal ultrafine particles to be used, from being eluded is favorably utilized.

[0036] As for the organic solvent to be used for these two applications, different types of organic solvents may be used; however, a same type of the organic solvent is preferably

used. Further, the type of solvent is not particularly limited as long as the solvent can be used for the two applications; however, such a solvent as has unduly high solubility against a compound, such as an alkyl amine or the like, which forms the adhesion layer on the surface of each of the metal ultrafine particles to have high polarity which eliminates the adhesion layer on the surface of each of the metal ultrafine particles is not selected, but a non-polar solvent or a low-polar solvent is preferably selected. Further, in the method for forming the circuit pattern according to the invention, it is preferable that the organic solvent is, after being applied, relatively quickly evaporated at a temperature at which the electrically conductive metal paste is thermally cured and the organic solvent is, during such evaporation, thermally stable to such an extent as it is not thermally decomposed. Still further, when a fine line is formed in the applying step, since the electrically conductive metal paste is inject-applied in a fine droplet by utilizing the inkjet method, it is also necessary to maintain the electrically conductive metal paste in a liquid viscosity range which is favorable for such discharging. When easiness of handling is taken into consideration, non-polar solvents or low-polar solvents having a relatively high boiling point which are not easily evaporated at a temperature in the neighborhood of room temperature, such as terpineol, mineral spirit, xylene, toluene, ethyl benzene, mesitylene are

favorably utilized and, further, hexane, heptane, octane, decane, dodecane, cyclohexane, cyclooctane and the like can be used.

[0037] A quantity of each of such organic solvents is selected depending on a quantity of the thermosetting resin component, the organic acid anhydride, the derivative thereof, the organic acid or the like which the solvent dissolves. On this occasion, it is preferable that, ordinarily, the resin composition containing the organic solvent is contained in the range of from 50 parts by mass to 300 parts by mass, with the organic solvent being contained in the range of from 20 parts by mass to 270 parts by mass therein in the electrically conductive metal paste to be used for forming the circuit pattern, per 100 parts by mass of the metal ultrafine particles in each case. This resin composition can comprise the thermosetting resin as the thermosetting resin component and, optionally, a hardener, a curing accelerator, and other usually used additive components. For example, as the polymerization agent, a thermosetting resin which can thermally be polymerized by utilizing the organic acid anhydride or the derivative thereof is also preferable.

[0038] On this occasion, as for the metal ultrafine particles having a very small average particle diameter

contained in the electrically conductive metal paste, fine particles comprising one type of metal or fine particles comprising an alloy made of two or more types of metals selected from the group consisting of: gold, silver, copper, platinum, palladium, tungsten, nickel, tantalum, bismuth, lead, indium, tin, zinc, titanium, and aluminum can appropriately be selected in accordance with purposes thereof. For an ordinary purpose, fine particles comprising a metal which is inherently excellent in electric conductivity such as gold, silver, copper, platinum or the like are in many cases utilized. Further, in a case in which fine particles comprising an alloy are used, ordinarily, an effect of the invention is demonstrated by using an alloy having a melting point higher than the thermosetting temperature of the thermosetting resin component.

[0039] In the method for forming the circuit pattern according to the invention, the electrically conductive metal paste containing these components is inject-applied on a substrate as a minute droplet by utilizing the inkjet method such that an aimed pattern form is allowed to be plotted. In accordance with a minimum line width and a space between lines to be targeted, for example, an average diameter of a dot to be applied is selected so as to be in the range of from 10 μm to 20 μm whereupon a quantity of the minute droplet is spontaneously determined in accordance with such selection of

the average diameter of the dot. That is, when the minute droplet is discharged by utilizing the inkjet method, since the quantity of the minute droplet depends on performance of an inkjet printer head itself to be utilized, such printer head adapted for the aimed quantity of the droplet is selected and, then, used. For example, when the average quantity of the droplet is in the range of from 2 pl to 100 pl, an inner diameter of a discharge nozzle is appropriately selected corresponding to the quantity.

[0040] Further, it goes without saying that the electrically conductive metal paste which forms a coating layer can assume a style of plotting by utilizing the inkjet method after the electrically conductive metal paste is allowed to be in a state in which metal ultrafine particles having a very small average particle diameter are previously uniformly dispersed in the resin composition; however, it is also possible that, for example, a liquid in which the metal ultrafine particles are dispersed in an organic solvent and another liquid containing a component constituting any other resin composition are separately prepared and these liquids are individually applied in respective minute droplets and are, then, mixed to form a coating film of the electrically conductive metal paste. When a method for forming a coating film of the electrically conductive metal paste of such two-component mixing type is used, registry of respective discharge nozzles for these liquids

of the inkjet printer head is performed so as to attain a close contact/superposition between both droplets. Further, needless to say, quantities of droplets of respective liquids are adjusted such that individual components have desired content ratios in a state in which both liquids are mixed. Thereafter, the resultant mixture is heated to perform substantially same thermosetting of the thermosetting resin component and low-temperature baking/fusion of the metal ultrafine particles thereamong as in a case in which a pre-mixed one-component type electrically conductive metal paste is used.

[0041] Further, when the two-component mixing type electrically conductive metal paste is utilized, since a liquid in which the metal ultrafine particles are dispersed in the organic solvent and another liquid containing a component constituting any other resin composition are each individually inject-applied, it is necessary to select each liquid viscosity such that it comes to be in a range capable of appropriately discharging. In some cases, a total quantity of the organic solvents contained in both liquids is larger than that of the organic solvent contained in the one-component type electrically conductive metal paste. In such case, it is preferable to provide a step for evaporating the organic solvent so as to reduce the content ratio thereof to an appropriate level in a heating step which is performed either during or

after forming the coating film.

[0042] Further, in the inkjet printer head to be utilized, there are two methods, that is, a thermal method which discharges ink by making use of heat-bubbling and a piezo method which discharges ink by making use of a piezoelectric element; the method for forming the circuit pattern according to the invention can use any one of the thermal method and the piezo method in performing plotting by inject-applying a metal fine particle paste to be used in a dot manner. It is necessary to prepare the liquid viscosity of the electrically conductive metal paste to be utilized depending on the method of the inkjet printer head to be utilized; for example, it is desirable that a final liquid viscosity is selected by adjusting a quantity of the organic solvent to be added such that it comes to be in the range of from 0.5 Pa·s to 30 Pa·s and preferably in the range of from 1 Pa·s to 5 Pa·s. Further, when the thermal method is utilized, it is necessary to select an organic solvent capable of performing the heat-bubbling, specifically, an organic solvent having a boiling point lower than a heating temperature of the thermal method.

[0043] In the method for forming the circuit pattern according to the invention, the electrically conductive metal paste so selected as to have a composition suitable for

utilization of the inkjet method is loaded in a liquid reservoir (container) of the inkjet printer head and, then, applied in the minute dot manner such that such dots are superposed with one another, thereby forming the circuit of from a desired minimum line width to a wide range of pattern with constant precision regardless of a shape of the pattern. Further, in regard also to a circuit film thickness to be formed, there is a merit in that the film thickness can be selected with a high degree of freedom by coating a plurality of layers. Still further, even when a region having a different designed film thickness is present in the circuit pattern to be produced in a same step, the region can be formed with same precision.

[0044] On the other hand, when the electrically conductive metal paste to be loaded in the liquid reservoir (container) of the inkjet printer head is left at room temperature or stored, since a reaction between the organic acid anhydride or the like and the terminal amino group of the compound which covers the surfaces of the metal fine particles does not substantially proceed at a temperature in the range of a conceivable maximum temperature, due to the feature that the thermosetting resin component contained in the electrically conductive metal paste according to the invention is thermally cured, unless the electrically conductive metal paste according to the invention is heated up to a predetermined temperature, a molecular layer

of the amine compound or the like which densely covers the surfaces of the metal ultrafine particles is maintained in a stable manner. By such action, agglomeration resistance at the time of storage is maintained to a great extent and a spontaneous formation of an oxide film on the surfaces of the metal ultrafine particles to be caused by moisture or oxygen in the air is suppressed. Further, since a uniform dispersion state of the contained metal ultrafine particles is maintained until they are discharged, a variation of the quantity of the coating droplet due to adhesion thereof to a discharging nozzle portion is not generated and also a variation of dispersion density due to agglomerate-separation or precipitation is not generated.

[0045]

[Example] An embodiment is given below to more specifically explain the invention. Although the embodiment is an example of the best mode of embodiments according to the invention, the invention is not limited thereto.

[0046] (Example 1) By utilizing a commercial dispersion of ultrafine particles of silver (trade name: INDEPENDENTLY DISPERSED ULTRAFINE PARTICLE "PERFECT SILVER"; available from Vacuum Metallurgical Co., Ltd.), specifically, a dispersion of silver fine particles having an average particle diameter

of 8 nm comprising 100 parts by mass of silver fine particles, 15 parts by mass of dodecyl amine as an alkyl amine, and 75 parts by mass of terpineol as an organic solvent, an electrically conductive metal paste (ink) of silver ultrafine particles was prepared.

[0047] The electrically conductive metal ink was prepared such that the dispersion of silver fine particles and, as individual components constituting a resin composition per 100 parts by mass of silver fine particles in the dispersion, 6.8 parts by mass of methyl hexahydrophthalic acid anhydride (Me-HHPA) as an acid anhydride, 5 parts by mass of a resol-type phenolic resin (trade name: PL-2211; available from Gunei Chemical Industry Co., Ltd.) as a thermosetting resin, and 35 parts by mass of toluene as an organic solvent were mixed and stirred in an aim for homogenization. The thus-prepared electrically conductive metal ink, after the silver fine particles were allowed to be in a state of being uniformly dispersed in the resin composition, was filtered by a filter made of polytetraethylene having a mesh size of 0.5 μm and, then, subjected to a treatment for removing an entrapped air. A liquid viscosity of the resultant electrically conductive metal ink is 10 Pa·s.

[0048] Next, the electrically conductive metal ink which

has been subjected to such air-bubble removal treatment was filled in an ink cartridge of a print head of an inkjet method. The print head filled with the electrically conductive metal ink was attached to a dedicated printer. In the present embodiment, respective printable properties of the print head of the inkjet method by a thermal method and a piezo method were inspected. Respective average quantities of droplets to be injected by the thermal method and the piezo method were 4 pl and 4 pl, respectively. By inject-applying these droplets, prints having average outer diameters of 16 μm and 18 μm in a dot shape become possible. In each of the thermal method and the piezo method, a straight line pattern having a film thickness of 5 μm and a line width of 100 μm was printed on a glass substrate by using the electrically conductive metal ink by the inkjet method. After such printing was performed, the electrically conductive metal ink on the glass substrate was subjected to a 2-stage thermal treatment, that is, heating at 150°C for 30 minutes and, then, further heating at 210°C for 60 minutes to perform curing of the contained thermosetting resin.

[0049] After such thermosetting treatment was performed, shapes/sizes such as the line width, a space between lines, surface flatness after the thermal treatment, and the film thickness were measured and the printability was evaluated.

Reproducibility of a shape/size of a plotted pattern was extremely high and has no deviation from the target, thereby being stable. More specifically, under the condition that densities (resolution) of prints in dot shapes in the thermal method and the piezo method were 600 dpi (dot/inch) and 720 dpi (dot/inch) respectively, the deviation of the line width was 10% or less at the maximum in terms of the dot diameter in each method; further, although some degrees of contraction was noticed along with the thermo-setting, the average film thickness was 3 μm and the variation of the film thickness was 20% or less. Still further, clogging of the discharge nozzle of the print head used by the inkjet method was not generated by the electrically conductive metal ink at all. Furthermore, specific resistance of a metal wiring pattern obtained by the 2-stage thermal treatment showed such a good value as being 2.8×10^{-5} Ω·cm with high reproducibility.

[0050]

[Advantage of the Invention] In the method for forming the circuit pattern by utilizing the inkjet method according to the invention, when the circuit pattern is plot-formed on a wiring substrate by using an electrically conductive metal paste, the electrically conductive metal paste to be used is a type of electrically conductive metal paste in which metal ultrafine particles having a very small average particle diameter are

uniformly dispersed in a resin composition, the metal ultrafine particles are selected such that an average particle diameter thereof comes to be in the range of from 1 nm to 100 nm, and a surface of each of the metal ultrafine particles is allowed to be in a state in which it is covered by at least one type of compound containing a group having nitrogen, oxygen and sulfur atoms as a group capable of bonding with a metal element contained in the metal ultrafine particles in a coordinate manner; on the other hand, the resin composition comprises a thermosetting resin component which, when heated, functions as an organic binder, a component having reactivity with the group having the nitrogen, oxygen and sulfur atoms, for example, an organic acid anhydride, a derivative thereof, or an organic acid and at least one type of organic solvent whereupon the circuit pattern is formed by the steps of:

plotting the circuit pattern by inject-applying the electrically conductive metal paste in small droplets on a substrate by a plotting means of the inkjet method;

thermally treating a coating layer of the thus-plotted electrically conductive metal paste at least at a temperature at which the thermosetting resin is thermally cured; and

forming the circuit pattern: as a result, there is a merit in that, along with thermally curing the thermosetting resin component, a molecular layer of the compound which covers the surface of each of the metal ultrafine particles is removed

by a reaction with, for example, the organic acid anhydride, the derivative thereof or the organic acid to allow the metal ultrafine particles to be fused thereamong at a low temperature, thereby forming an electrically conductive layer in a network shape having a close electric contact whereupon, along with utilization of the metal ultrafine particles, a pattern of a fine line width can be produced with high precision and also the wiring circuit showing excellent electric conductivity can be produced with high reproducibility. Further, along with the use of the electrically conductive metal paste having the constitution described above, high conduction stability and reproducibility, which can not be obtained by a conduction path generated by a contact of particles themselves, can be secured and, further, since a resin which is thermally cured is contained therein, an ultrafine circuit which has excellent adhesion strength to the substrate and also no substantial variation in the film thickness can conveniently be print-produced.

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F Term (reference)

2C056 EA04 FA03 FA04 FB05

4J038 CF001 DA041 DA101 DA141

DA161 DB001 DD181 DJ021

DL031 GA02 GA08 GA13

HA066 JA02 JA03 JA12

JA37 JA39 JB03 JC02 JC12

KA03 KA06 KA08 KA20 NA20

PA19 PB09 PC03 PC08

5E343 BB22 BB23 BB24 BB25 BB28

BB34 BB40 BB44 BB48 BB49

BB72 BB76 DD14 ER33 ER39

FF02 GG02